Synthesis of Indeno-Fused Derivatives of Quinolizinium Salts, Imidazo[1,2-*a*]pyridine, Pyrido[1,2-*a*]indole, and 4*H*-Quinolizin-4-one via Benzannulated Enyne–Allenenes

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Supporting Information

Table of Contents

Page	
S5	General Experimental Methods
S5	Experimental Procedure for Pyridinium Methanesulfonate 11b .
S5	Experimental Procedure for Pyridinium Methanesulfonate 11c .
S6	Experimental Procedure for 2-(Dimethylamino)-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15b).

S6	Experimental Procedure for 2-Methoxy-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15c).
S7	Experimental Procedure for Propargyl Methanesulfonate 18b .
S7	Experimental Procedure for Pyridinium Methanesulfonate 19b .
S7	Experimental Procedure for 2-(Dimethylamino)-12-(trimethylsilyl)-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Chloride (21b).
S9–S10	¹ H and ¹³ C NMR Spectra of Propargylic Alcohol 8 .
S11–S12	¹ H and ¹³ C NMR Spectra of Propargyl Methanesulfonate 9 .
S13–S14	¹ H and ¹³ C NMR Spectra of Pyridinium Methanesulfonate 11a .
S15–S16	¹ H and ¹³ C NMR Spectra of Pyridinium Methanesulfonate 11b .
S17–S18	¹ H and ¹³ C NMR Spectra of Pyridinium Methanesulfonate 11c .
S19–S20	¹ H and ¹³ C NMR Spectra of 2-Amino-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15a).
S21–S22	¹ H and ¹³ C NMR Spectra of 2-(Dimethylamino)-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15b).
S23–S24	¹ H and ¹³ C NMR Spectra of 2-Methoxy-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15c).
S25–S26	¹ H and ¹³ C NMR Spectra of Propargylic Alcohol 17a .
S27–S28	¹ H and ¹³ C NMR Spectra of Propargyl Methanesulfonate 18a .
S29–S30	¹ H and ¹³ C NMR Spectra of Propargyl Methanesulfonate 18b .

S31–S32	^1H and ^{13}C NMR Spectra of Pyridinium Methanesulfonate 19a .
S33–S34	^1H and ^{13}C NMR Spectra of Pyridinium Methanesulfonate 19b .
S35–S36	^1H and ^{13}C NMR Spectra of 2-(Dimethylamino)-12-(1,1-dimethylethyl)-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Chloride (21a).
S37–S38	^1H and ^{13}C NMR Spectra of 2-(Dimethylamino)-12-(trimethylsilyl)-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Chloride (21b).
S39–S40	^1H and ^{13}C NMR Spectra of 11-Phenyl-6 <i>H</i> -indeno[1,2- <i>d</i>]imidazo[1,2- <i>a</i>]pyridine (24).
S41–S42	^1H and ^{13}C NMR Spectra of Indole 31 .
S43–S44	^1H and ^{13}C NMR Spectra of 12-Phenyl-7 <i>H</i> -indeno[1',2':4,5]pyrido[1,2- <i>a</i>]indole (32).
S45–S46	^1H and ^{13}C NMR Spectra of 2(1 <i>H</i>)-Pyridinone 34 .
S47–S48	^1H and ^{13}C NMR Spectra of 4,7-Dihydro-12-phenylindeno[2,1- <i>g</i>]quinolizin-4-one (35).
S49	Figure S1. ORTEP Drawing of the Crystal Structure of 2-Amino-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15a).
S50	Figure S2. ORTEP Drawing of the Crystal Structure of 2-(Dimethylamino)-12-phenyl-7 <i>H</i> -indeno[1,2- <i>b</i>]quinolizin-5-ium Methanesulfonate (15b).

- S51 Figure S3. ORTEP Drawing of the Crystal Structure of
2-Methoxy-12-phenyl-7*H*-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (**15c**).
- S52 Figure S4. ORTEP Drawing of the Crystal Structure of
2-(Dimethylamino)-12-(1,1-dimethylethyl)-7*H*-indeno[1,2-*b*]quinolizin-5-ium
Chloride (**21a**).
- S53 Figure S5. ORTEP Drawing of the Crystal Structure of
11-Phenyl-6*H*-indeno[1,2-*d*]imidazo[1,2-*a*]pyridine (**24**).
- S54 Figure S6. ORTEP Drawing of the Crystal Structure of
4,7-Dihydro-12-phenylindeno[2,1-*g*]quinolizin-4-one (**35**).

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether was distilled from benzophenone ketyl. Compounds **6**,^{3c} **16**,⁹ **17b**,⁹ **25**,¹⁰ **30**,¹⁰ and **33**¹⁰ were prepared according to the reported procedures. 4-Aminopyridine, 4-(dimethylamino)pyridine, 4-methoxypyridine, 2.5 M solution of butyllithium in hexanes, propargyl alcohol, Pd(PPh₃)₂Cl₂, copper(I) iodide, methanesulfonyl chloride, 3,3-dimethyl-1-butyne, (trimethylsilyl)ethyne, imidazole, tetrabutylammonium iodide, 1.0 M solution of potassium *t*-butoxide in *t*-butyl alcohol were purchased from chemical suppliers and were used as received. Melting points were uncorrected. ¹H (270 MHz) and ¹³C (67.9 MHz) NMR spectra were recorded in CDCl₃ using CHCl₃ (¹H δ 7.26) and CDCl₃ (¹³C δ 77.00) as internal standards unless otherwise indicated.

Pyridinium Methanesulfonate 11b. To a solution of **9** (186 mg, 0.600 mmol) in 5 mL of methylene chloride was added dropwise a solution of 4-(dimethylamino)pyridine (73 mg, 0.60 mmol) in 5 mL of methylene chloride. The reaction mixture was stirred at room temperature for 24 h and concentrated. The residue was washed with diethyl ether to give 259 mg (0.600 mmol, 100%) of **11b** as a viscous liquid: IR 1651, 1192, 765 cm⁻¹; ¹H δ 8.64 (2 H, d, *J* = 7.9 Hz), 7.46–7.57 (4 H, m), 7.29–7.42 (5 H, m), 6.51 (2 H, d, *J* = 7.9 Hz), 5.53 (2 H, s), 3.07 (6 H, s), 2.81 (3 H, s); ¹³C δ 156.2, 141.6, 131.8, 131.7, 129.0, 128.7, 128.5, 128.3, 125.5, 123.5, 122.6, 107.7, 93.0, 88.4, 87.9, 83.7, 47.5, 40.1, 39.5.

Pyridinium Methanesulfonate 11c. To a solution of **9** (30 mg, 0.097 mmol) in 5 mL of methylene chloride was added dropwise a solution of 4-methoxypyridine (11 mg, 0.101 mmol) in 5 mL of methylene chloride. The reaction mixture was stirred at room temperature for 24 h and concentrated. The residue was washed with diethyl ether to give 41 mg (0.097 mmol, 100%) of **11c** as a colorless solid: mp 133–134 °C; IR 2216, 1192, 762 cm⁻¹; ¹H δ 9.19 (2 H, d, *J* = 6.9

Hz), 7.31–7.55 (9 H, m), 6.99 (2 H, d, $J = 6.9$ Hz), 5.86 (2 H, s), 3.96 (3 H, s), 2.78 (3 H, s); ^{13}C δ 171.1, 145.7, 131.9, 131.7, 129.3, 128.9, 128.7, 128.5, 128.4, 125.7, 123.2, 122.6, 113.2, 93.0, 89.8, 87.9, 82.7, 57.8, 49.9, 39.5.

2-(Dimethylamino)-12-phenyl-7H-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (15b).

A solution of **11b** (51 mg, 0.12 mmol) and triethylamine (12 mg, 0.12 mmol) in 10 mL of ethanol was stirred at room temperature for 72 h. The solvent was removed and the residue was washed with diethyl ether to give 51 mg (0.12 mmol, 100%) of **15b** as a yellow solid: compound

becomes black at 228 °C without melting; IR 1647, 1195 cm^{-1} ; ^1H δ 9.62 (1 H, d, $J = 7.6$ Hz), 9.39 (1 H, s), 7.61–7.71 (3 H, m), 7.55 (1 H, d, $J = 7.7$ Hz), 7.26–7.41 (4 H, m), 7.07 (1 H, t, $J = 7.9$ Hz), 6.43 (1 H, d, $J = 8.2$ Hz), 6.27 (1 H, d, $J = 2.9$ Hz), 4.22 (2 H, s), 3.04 (6 H, s), 2.87 (3 H, s); ^{13}C δ 152.0, 146.3, 145.7, 143.8, 138.8, 136.8, 133.9, 132.4, 131.0, 130.3, 130.1, 129.7, 129.2, 127.4, 126.6, 125.6, 125.3, 109.8, 99.6, 39.7, 39.6, 34.3. Recrystallization of **15b** from a mixture of dichloromethane and hexanes produced a crystal suitable for X-ray structure analysis.

2-Methoxy-12-phenyl-7H-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (15c).

A solution of **11c** (150 mg, 0.358 mmol) and triethylamine (36 mg, 0.36 mmol) in 40 mL of ethanol was stirred at room temperature for 15 h. The solvent was removed and the residue was washed with diethyl ether to give 150 mg (0.358 mmol, 100%) of **15c** as a yellow solid: compound becomes black at 228 °C without melting; IR 1644, 1193 cm^{-1} ; ^1H δ 10.09 (1 H, s), 9.99 (1 H, d, $J = 7.7$ Hz), 7.69–7.78 (3 H, m), 7.64 (1 H, d, $J = 7.9$ Hz), 7.37–7.52 (4 H, m), 7.14 (1 H, t, $J = 7.8$ Hz), 6.87 (1 H, d, $J = 3.0$ Hz), 6.52 (1 H, d, $J = 8.2$ Hz), 4.39 (2 H, s), 3.86 (3 H, s), 2.92 (3 H, s); ^{13}C δ 163.8, 148.0, 146.9, 144.5, 140.3, 136.4, 136.2, 133.1, 132.3, 131.9, 130.5, 130.1, 129.2, 127.9, 127.7, 125.8, 125.6, 114.4, 103.2, 56.6, 39.6, 34.8. Recrystallization of **15c** from a mixture of dichloromethane and hexanes produced a crystal suitable for X-ray structure analysis.

Propargyl Methanesulfonate 18b. To a solution of **17b** (164 mg, 0.72 mmol) and triethylamine (109 mg, 1.08 mmol) in 10 mL of methylene chloride at $-50\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere was added dropwise methanesulfonyl chloride (108 mg, 0.94 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h before 5 mL of water was introduced. The organic layer was separated, and the aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over MgSO_4 , and concentrated. The residue was purified by column chromatography (silica gel/ethyl acetate:hexanes = 1:4) to give 196 mg (0.64 mmol, 89%) of **18b** as a colorless liquid: IR 2232, 2159, 1367, 1177 cm^{-1} ; ^1H δ 7.41–7.50 (2 H, m), 7.25–7.35 (2 H, m), 5.12 (2 H, s), 3.17 (3 H, s), 0.27 (9 H, s); ^{13}C δ 132.4, 132.2, 129.1, 128.3, 126.1, 124.0, 102.7, 99.4, 87.9, 84.4, 58.4, 39.3, -0.1 .

Pyridinium Methanesulfonate 19b. To a solution of **18b** (26 mg, 0.085 mmol) in 5 mL of methylene chloride was added dropwise a solution of 4-(dimethylamino)pyridine (10.4 mg, 0.085 mmol) in 5 mL of methylene chloride. The reaction mixture was stirred at room temperature for 24 h and concentrated. The residue was washed with diethyl ether to give 36 mg (0.084 mmol, 99%) of **19b** as a colorless solid: compound becomes black at $162\text{ }^{\circ}\text{C}$ without melting; IR 2158, 1652, 1194 cm^{-1} ; ^1H δ 8.61 (2 H, d, $J = 7.4\text{ Hz}$), 7.43–7.49 (2 H, m), 7.28–7.34 (2 H, m), 6.97 (2 H, d, $J = 7.7\text{ Hz}$), 5.48 (2 H, s), 3.25 (6 H, s), 2.79 (3 H, s), 0.21 (9 H, s); ^{13}C δ 156.6, 141.9, 132.5, 132.4, 129.1, 128.4, 125.7, 123.5, 108.1, 103.0, 98.9, 88.3, 83.2, 47.8, 40.3, 39.5, 0.0.

2-(Dimethylamino)-12-(trimethylsilyl)-7H-indeno[1,2-*b*]quinolizin-5-ium Chloride (21b). A solution of **19b** (30 mg, 0.070 mmol) and triethylamine (7 mg, 0.07 mmol) in 10 mL of ethanol was heated under reflux for 48 h. The solvent was removed in vacuo, and the residue was

purified by column chromatography (neutral alumina/ethanol:methylene chloride = 1:10) to give 11 mg (0.030 mmol, 43%) of **21b** as a yellow solid: mp > 360 °C; IR 1646, 1235 cm⁻¹; ¹H δ 10.16 (1 H, d, *J* = 7.6 Hz), 9.70 (1 H, s), 7.93 (1 H, d, *J* = 7.6 Hz), 7.62 (1 H, d, *J* = 7.6 Hz), 7.40–7.56 (3 H, m), 7.21 (1 H, dd, *J* = 7.6, 2.9 Hz), 6.98 (1 H, d, *J* = 2.6 Hz), 4.15 (2 H, s), 3.26 (6 H, s), 0.62 (9 H, s); ¹³C δ 157.1, 151.4, 147.0, 146.6, 139.2, 138.2, 132.6, 131.2, 130.5, 127.7, 126.7, 125.9, 125.3, 109.2, 103.2, 40.1, 34.5, 2.6.

Figure S1. ORTEP Drawing of the Crystal Structure of 2-Amino-12-phenyl-7*H*-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (**15a**).

Figure S2. ORTEP Drawing of the Crystal Structure of 2-(Dimethylamino)-12-phenyl-7*H*-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (**15b**).

Figure S3. ORTEP Drawing of the Crystal Structure of 2-Methoxy-12-phenyl-7*H*-indeno[1,2-*b*]quinolizin-5-ium Methanesulfonate (**15c**).

Figure S4. ORTEP Drawing of the Crystal Structure of 2-(Dimethylamino)-12-(1,1-dimethylethyl)-7H-indeno[1,2-b]quinolizin-5-ium Chloride (**21a**).

Figure S5. ORTEP Drawing of the Crystal Structure of 11-Phenyl-6H-indeno[1,2-d]imidazo[1,2-a]pyridine (24).

Figure S6. ORTEP Drawing of the Crystal Structure of
4,7-Dihydro-12-phenylindeno[2,1-g]quinolin-4-one (35).